Chemistry of Ylides. XX. Triphenylarsonium Phenacylide

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Triphenylarsonium phenacylide (I) has been prepared by two routes, and its chemical properties have been studied. It undergoes hydrolysis, thermal decomposition, O-alkylation, and C- or O-acylation. Reaction with carbonyl compounds normally affords olefins by ylide attack on the carbonyl carbon but with α,β-unsaturated carbonyl compounds a Michael addition occurs affording cyclopropanes.

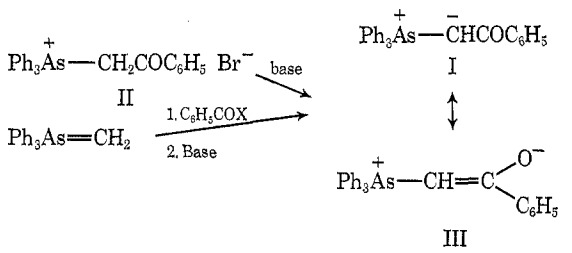
Although the first arsonium ylide appears to have been prepared in 1902[1] but not assigned its correct structure until 1950,[2] no more than 11 references were cited in the most recent (1966) review of arsenic ylide chemistry.[3] By now approximately 16 different arsonium ylides have been prepared but only about half have been isolated. As was pointed out in 1966,[3] and as remains true today, very little is known of the general chemistry and physical properties of arsonium ylides. This is in contrast with the large amount of information available for ylides of sulfur and phosphorus.

Interest in the chemistry of the ylides of arsenic continues because, based on the meager information presently available, arsenic seems to lie between sulfur and phosphorus in its effect on the properties of ylides. A study of arsenic ylide chemistry may discover unique chemical or physical properties and/or shed light on the mechanism of reactions of phosphorus or sulfur ylides, both of which results would have recognized importance in preparative organic chemistry.

This report relates some of the general chemistry of triphenylarsonium phenacylide (I), a stable, isolable arsenic ylide. It lays the base for further detailed studies of such ylides and their reactions.

Results and Discussion

Quaternization of triphenylarsine with phenacyl bromide afforded the known[3,4] arsonium salt II. Treatment of this salt with sodium ethoxide in benzene effected the proton abstraction and afforded the crystalline ylide I of mp 172–173°. Prior reports quoted melting points ranging from 154 to 183°.[2,5,6] The ylide I also could be prepared by acylating triphenylarsonium methylide with benzoyl chloride, benzoic anhydride, or ethyl benzoate.



The carbonyl absorption for the ylide salt II was at 1660 cm^{-1} whereas that for the ylide was at 1570 cm^{-1}, indicating a significant contribution of the enolate structure III and accounting for some of the stability of the ylide. The nuclear magnetic resonance (nmr) spectrum showed 20 aryl protons at δ 7.2–8.1 and the single methine proton at δ 4.75. The methine absorption was quite broad unless the sample and the solvent were especially dry, probably owing to proton exchange. Recently we reported such exchange for the analogous phosphonium ylide.[7]

The ylide I was stable to the atmosphere. However, warming the ylide in aqueous ethanol led to hydrolysis to triphenylarsine oxide and acetophenone, a cleavage typical of phosphonium ylides.[8] Treatment of a solution of the ylide with oxygen over extended periods of time resulted in no reaction but treatment with ozone resulted in oxidative cleavage to triphenylarsine oxide and phenyl glyoxal. Accordingly, the ylide seemed to show a sensitivity to hydrolysis and oxidation virtually identical with that shown by triphenylphosphonium phenacylide.[8]

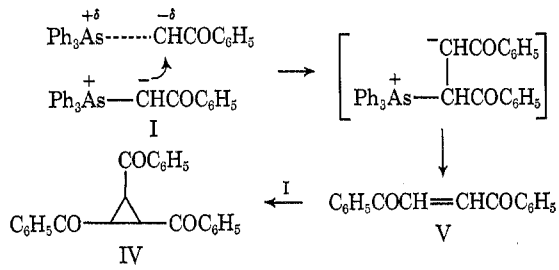
The thermal stability of the ylide I was investigated. Heating the pure ylide to 200° led to decomposition with triphenylarsine being the only identifiable product. The ylide could be recovered unchanged after extended heating in benzene solution but on heating in toluene solution, with or without the presence of copper sulfate, a high yield of *trans*-1,2,3-tribenzoylcyclopropane (IV) and triphenylarsine could be obtained. In this behavior the arsonium ylide I was identical with the analogous sulfonium phenacylide[9] but different from the phosphonium phenacylide which was stable to these conditions.

To account for the decomposition we propose the ylide commenced to dissociate *via* a carbenoid intermediate which quickly was attacked by another nucleophilic ylide molecule (Scheme I). The resulting betaine would eliminate triphenylarsine to afford 1,2-dibenzoylethene (V). Michael addition of additional ylide I to the olefin V would afford the observed product IV. In a separate experiment the latter reaction was found to proceed rapidly and quantitatively. However, an attempt to trap the olefin V with 2,5-diphenylisobenzofuran in a decomposition reaction failed.

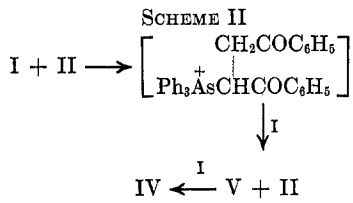
An alternative mechanism which must be considered is shown in Scheme II. This proposal involves essentially a chain reaction with a minute amount of ylide salt II formed from any source, perhaps even by reaction of traces of water with ylide, serving as the chain-carrying agent. This mechanism was shown to

(1) A. Michaelis, *Justus Liebigs Ann. Chem.*, **321**, 174 (1902).
(2) F. Krohnke, *Chem. Ber.*, **83**, 291 (1950).
(3) A. Wm. Johnson, "Ylid Chemistry," Academic Press, New York and London, 1966, pp 288–299.
(4) G. Aksnes and J. Songstad, *Acta Chem. Scand.*, **18**, 655 (1964).
(5) N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **155**, 1364 (1964).
(6) N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, *Izv. Akad. Nauk SSSR*, 1474 (1965).
(7) F. J. Randall and A. Wm. Johnson, *Tetrahedron Lett.*, 2841 (1968).
(8) F. Ramirez, R. B. Mitra, and N. B. Desai, *J. Amer. Chem. Soc.*, **82**, 5763 (1960).
(9) Paper XIX in this series: A. W. Johnson and R. T. Amel, *J. Org Chem.*, **34**, 1240 (1969).

SCHEME I

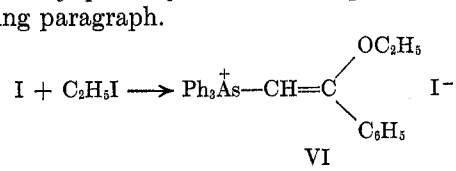


SCHEME II

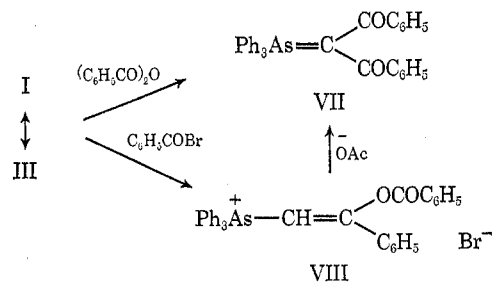


be possible by the observation that reaction of the ylide I with phenacyl bromide or with the conjugate acid of the ylide did afford the cyclopropane IV. There appears to be no simple means, perhaps other than a kinetic study, of distinguishing between the two possible mechanisms.[10]

The nucleophilic character of the ylide I was demonstrated by its undergoing an alkylation. Reaction with ethyl iodide afforded the O-ethyl product VI, the structure of which was proven by ir and nmr spectra and by hydrolysis to triphenylphenacylarsonium iodide. This result is identical with the O-alkylation found for the phosphonium phenacylide[11] but contrasts with the C-alkylation we reported for the sulfonium phenacylide.[9] Furthermore, it contrasts with the apparent C-alkylation of I by phenacyl bormide as postulated in the preceding paragraph.



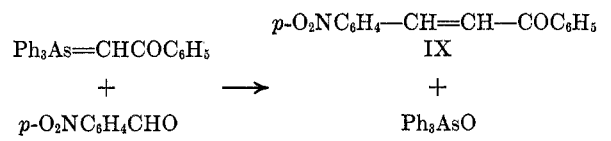
The ylide I also underwent acylation, the course of which depended on the reagent used. Reaction with benzoic anhydride afforded dibenzoylmethylenetriphenylarsenane (VII), presumably *via* initial C-benzoylation followed by proton abstraction from the new arsonium salt. The dibenzoylmethyltriphenylarsonium salt would be the most acidic species present and could suffer loss of a proton to the benzoate ion or to ylide I, thereby affording the new, highly stabilized ylide VII. Similar behavior was observed using acetic anhydride, benzoylacetylmethylenetriphenylarsenane being the product.



(10) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **83**, 4033 (1961).
(11) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

Benzoylation of the ylide I with benzoyl bromide effected an O-acylation affording the enol benzoate VIII. The structure of VIII was proven by its ir spectrum (ν_{CO} 1745 cm^{-1}), the nmr spectrum showing a methine proton (δ 6.45 ppm), and by isomerization of VIII to the C-benzoylated product VII in the presence of sodium acetate. This rearrangement probably involves conversion of a kinetically controlled product VIII to the thermodynamically controlled product VII as was reported for the triphenylphosphonium phenacylide system.[12]

One of our major interests in exploring arsonium ylide chemistry is to ascertain how such ylides react with carbonyl compounds. Phosphonium ylides have long been known to afford olefins in such reactions (Wittig Reaction), presumably *via* a betaine adduct X intermediate.[13] Sulfonium ylides have been shown to afford epoxides under similar conditions, presumably *via* a similar intermediate.[14] Based on the few reports[15] to date on their reaction in which either olefin, epoxide, or both are formed upon reaction with carbonyl compounds, arsonium ylides seem intermediate in character between phosphonium and sulfonium ylides. Preparatory to exploring this unique position in depth, we have observed that triphenylarsonium phenacylide (I) reacts with *p*-nitrobenzaldehyde to form exclusively the olefinic product, *trans*-*p*-nitrobenzalacetophenenone (IX), and triphenylarsine oxide in high yield with no evidence of the formation of an epoxide or an arsine.

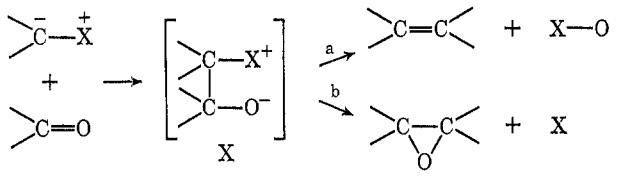


The results to date indicate that stabilized arsonium ylides, such as the phenacylide, carbomethoxymethylide,[15b] fluorenylide,[15c] and cyclopentadienylide,[15e] afford only olefinic products upon reaction with carbonyl compounds. The nonstabilized arsonium ylides, such as the methylide[15a] and ethylide,[15f] afforded almost exclusively epoxides (or products resulting from their rearrangement). However, a semistabilized arsonium ylide, the benzylide,[15d] has afforded approximately equimolar amounts of epoxide and olefin. Clearly, the nature of the carbanion fragment of the arsonium ylide is having a major influence on the course of the reaction. It is reasonable to suppose a two-step mechanism (Scheme III) is involved in the reactions of phosphonium, sulfonium, and arsonium ylides with carbonyl compounds. Therefore, since the product-determining step must be the second step in such a mechanism, the nature of the carbanion substituent must be affecting that step in an important manner.

No evidence is available to indicate how the carbanion substituent in arsonium ylides affects the distribution between path a and path b in Scheme III. It is conceivable that the "normal" path is b since triphenylarsine is not an especially strong oxygen scavenger as is

(12) P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *ibid.*, **30**, 1015 (1965).
(13) Reference 3, pp 132–192.
(14) Reference 3, pp 304–366.
(15) (a) M. C. Henry and G. Wittig, *J. Amer. Chem. Soc.*, **82**, 563 (1960); (b) Y. T. Huang, W. Y. Ting, and H. S. Cheng, *Acta Chim. Sinica*, **31**, 37 (1965); (c) A. Wm. Johnson, *J. Org. Chem.*, **25**, 183 (1960); (d) A. W. Johnson and J. O. Martin, *Chem. Ind.* (London), 1726 (1965); (e) D. Lloyd and M. I. C. Singer, *ibid.*, 510 (1967). (f) A. Maccioni and M. Secci, *Chem. Abstr.*, **63**, 5674 (1965).

SCHEME III



triphenylphosphine. However, with the presence of a conjugating group on one of the carbon atoms of the betaine X, sufficient stabilization may be provided for the incipient double bond in the transition state for path a to increase the ratio of path a product to path b product. We are exploring the nature of this reaction further.

Experimental Section

Triphenylarsonium Phenacylide (I).—A homogeneous solution of 6.1 g (20 mmol) of triphenylarsine and 4.4 g (22 mmol) of phenacyl bromide in 30 ml of benzene was heated under reflux for 4 hr. The resulting precipitate of 6.2 g (56%) of phenacyltriphenylarsonium bromide (II) was removed by filtration and a sample was recrystallized from chloroform–benzene to mp 185° (lit.[4] mp 186°): ν_{CO} 1660 cm^{-1}; nmr absorption at δ 6.45 (area 2.0, methylene singlet) and 7.3–8.3 (area 20.7, aromatic multiplet).

To a solution of 0.9 g (2 mmol) of methyltriphenylarsonium iodide (prepared from methyl iodide and triphenylarsine) in 40 ml of benzene was added 10 mmol of potassium *t*-butoxide. After stirring for 10 min 0.3 g (2 mmol) of ethyl benzoate was added to the yellow solution. After stirring for 1 hr the excess butoxide was decomposed with ethanol, and the reaction was flooded with water and then acidified with hydrobromic acid. Extraction with chloroform and then evaporation of this solvent afforded 0.5 g (50%) of crude arsonium salt II which showed mp 180–182° after one crystallization.

To a slurry of 11 g (22 mmol) of II in 100 ml of dry benzene containing 0.5 ml of absolute ethanol was added 5 g of sodium hydride in mineral oil (50% slurry). After stirring overnight most of the solid material had dissolved and the solution had become a deep yellow color. The remaining precipitate was removed by filtration after which the filtrate was diluted with hexane to precipitate 9 g (95%) of the ylide I. The ylide was recrystallized from benzene–hexane as pale yellow microcrystals: mp 172–173° (lit.[2] mp 182–183°; lit.[5] mp 154–156°; lit.[6] mp 167–169°); ν_{CO} 1570 cm^{-1}; nmr absorption in alumina-dried $CDCl_3$ at δ 4.75 (area 1, methine singlet of half-width 1 cps) and 7.2–8.1 (area 20.2, aromatic multiplet). The methine singlet for a twice-recrystallized sample had a half-width of 4 cps unless the $CDCl_3$ first was shaken with alumina.

Warming a solution of 0.85 g of ylide I in 10 ml of aqueous ethanol and then extraction with chloroform left no organic matter in the aqueous phase. Evaporation of the chloroform and extraction of the oily residue with pentane afforded a solution of acetophenone as identified by infrared comparison with an authentic sample. The pentane-insoluble material was identified as triphenylarsine oxide by infrared spectral comparison with an authentic sample.

Ozonolysis of 0.85 g (2 mmol) of ylide I in 40 ml of methylene chloride at −70° led to the loss of the yellow color. The solvent was evaporated and a 2,4-dinitrophenylhydrazone was prepared in ethanolic solution. The red derivative crystallized from dimethylformamide–nitromethane, mp 292–294°, and appeared to be the bis-2,4-dinitrophenylhydrazone of phenyl glyoxal.

Anal. Calcd for $C_{20}H_{14}O_8N_8$: C, 48.59; H, 2.85; N, 22.66. Found: C, 48.66; H, 2.94; N, 22.30.

After the preparation of the derivative, triphenylarsine oxide was isolated from the filtrate by chromatography on alumina and was identified by melting point (197–198°) and comparison of its infrared spectrum with that of an authentic sample.

Thermolysis of Ylide I.—A solution of 4.2 g (1 mmol) of ylide I in 20 ml of toluene was heated under reflux for 2 days. During this time samples were withdrawn, and it was noted that the ylide carbonyl absorption at 1570 cm^{-1} gradually disappeared as a new carbonyl absorption at 1670 cm^{-1} gradually appeared and increased in intensity. Evaporation of the solvent and chromatography of the residue on alumina afforded 0.11 g (100%) of crude *trans*-1,2,3-tribenzoylcyclopropane (IV) which crystallized from benzene–heptane as colorless needles, mp 215° (lit.[16] mp 215°), ν_{CO} 1665 cm^{-1}, and was proven identical with an authentic sample by admixture melting point and comparison of infrared spectra.

A solution of 0.42 g (1 mmol) of ylide I and 0.24 g (1 mmol) of dibenzoylethylene in 20 ml of benzene was stirred for 24 hr at room temperature. Evaporation of the solvent and chromatography of the residue on alumina afforded a quantitative yield of IV.

To a stirred solution of 0.6 g (3 mmol) of phenacyl bromide in 30 ml of benzene was added 0.85 g (2 mmol) of ylide I. A precipitate began to form immediately and after 10 hr a total of 0.6 g of ylide salt II was obtained. Chromatography of the filtrate afforded 0.12 g of IV. Repetition of the reaction, but using the ylide salt II in place of the phenacyl bromide, again afforded the cyclopropane derivative IV.

Alkylation of Ylide I with Ethyl Iodide.—A solution of 1.3 g (3 mmol) of ylide I and 3 ml of ethyl iodide in 20 ml of methylene chloride was heated under reflux for 10 hr. Addition of ether afforded 1.3 g (75%) of crude β-(α-ethoxy)styryltriphenylarsonium iodide (VI) which was recrystallized from chloroform–ether as a colorless powder, mp 159–160°, $\nu_{C=C}$ 1590 cm^{-1}, with nmr absorption in $CDCl_3$ at δ 7.5–7.8 (area 20, aromatic multiplet), 5.78 (area 1, methine singlet), 3.66 (area 2, methylene quartet, J = 7 cps), 0.66 (area 3.1, methyl triplet, J = 7 cps). Use of a higher boiling solvent, such as benzene or toluene, in the alkylation also afforded some of the desired alkylation product VI but it was contaminated with considerable thermal decomposition product IV.

Anal. Calcd for $C_{28}H_{26}AsIO$: C, 57.95; H, 4.52; I, 21.87. Found: C, 57.86; H, 4.65; I, 21.94.

Hydrolysis of 0.4 g (0.7 mmol) of the alkylation product VI by warming in 20 ml of ethanol containing 5 ml of 47% hydriodic acid afforded 0.3 g (80%) of phenacyltriphenylarsonium iodide, mp 140°.

Acylation of Ylide I. A. With Benzoyl Bromide.—Addition of 0.2 g (1.1 mmol) of benzoyl bromide to 0.4 g (1 mmol) of ylide I in 10 ml of benzene resulted in the formation of an immediate precipitate (0.4 g, 70%) of the enol benzoate VIII. Crystallization from acetonitrile–ether gave colorless microcrystals, mp 179–180°, ν_{CO} 1745 cm^{-1}, $\nu_{C=C}$ 1620 cm^{-1}, with nmr absorption in $CDCl_3$ at δ 7.3–8.1 (aromatic multiplet) and 6.45 (methine singlet). Warming the benzoate with 1 g of sodium acetate in chloroform solution afforded 0.25 g of dibenzoylmethylenetriphenylarsenane (VII), mp 208–210°, shown to be identical with an authentic sample by admixture melting point and a comparison of infrared spectra.

B. With Benzoic Anhydride.—A mixture of 0.85 g (2 mmol) of ylide I and 0.45 g (2 mmol) of benzoic anhydride in 20 ml of benzene was stirred overnight. Evaporation of the solvent afforded an oil which crystallized from ether. Recrystallization from benzene–heptane gave 0.5 g (50%) of dibenzoylmethylenetriphenylarsenane (VII), mp 208–210°, ν_{CO} 1520 cm^{-1}, no aliphatic protons were visible in the nmr spectrum. A similar reaction with acetic anhydride gave benzoylacetylmethylenetriphenylarsenane, mp 174°, ν_{CO} 1520 cm^{-1}, with nmr absorption in $CDCl_3$ at δ 7.2–7.8 (area 20.2, aromatic multiplet) and 1.80 (area 3.0, methyl singlet).

Reaction of Ylide I with *p*-Nitrobenzaldehyde.—A solution of 0.85 g (2 mmol) of ylide I with 0.3 g (2 mmol) of *p*-nitrobenzaldehyde in 20 ml of benzene was stirred overnight during which time a yellow precipitate appeared. The precipitate was removed and the filtrate was chromatographed on alumina to afford additional yellow substance. The combined yellow products were crystallized from ethanol to afford 0.5 g (90%) of *p*-nitrobenzalacetophenone (IX), mp 164–165° (lit.[17] mp 160–161°).

Registry No.—I, 24904-06-1; VI, 24904-07-2; bis-(2,4-dinitrophenylhydrazone) of phenyl glyoxal, 4881-22-5.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(16) G. Maier, *Chem. Ber.*, **95**, 611 (1962).
(17) W. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, **75**, 5990 (1953).